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The Role of Dispersants in Oil Spill Remediation

Fundamental Concepts, Rationale for Use, Fate, and Transport Issues

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The crew of a Basler BT-67 fixed-wing aircraft releases oil dispersant over the Deepwater Horizon oil spill, offshore Louisiana. *US Coast Guard photo by Petty Officer 3rd Class Stephen Lehmann*

ABSTRACT. Offering a scientific perspective, this paper provides a rationale for the use of dispersants in oil spill remediation by discussing their formulations and modes of action and connecting their physics and chemistry to a their environmental fates and impacts. With the first use of dispersants at the source of the oil release during the Deepwater Horizon incident, there is a new great need for understanding the efficiency and the environmental impacts of their use. The paper concludes with some cautionary recommendations on dispersant research.

INTRODUCTION AND PHYSICOCHEMICAL ASPECTS OF DISPERSANT ACTION

Oil dispersants have been shown to break up surface oil slicks when applied under the appropriate conditions, leading to reduced oiling of beaches and shorelines (National Research Council, 2005). The DWH spill was unprecedented in that oil was being released ~1,600 m below the ocean's surface. Nevertheless, concerns about surface worker safety and oil on Gulf of Mexico beaches and marshes led to the decision to apply dispersants at the surface as well as at depth during the DWH spill. Over the course of the spill, 2.9 million liters of dispersant were applied at depth, and 4.1 million liters were applied at the surface (Place et al., 2016). Early in the spill, the dispersant Corexit 9527 was the primary formulation, but it was replaced with Corexit 9500 once sufficient supplies were available (National Commission on the BP Deepwater Horizon Oil Spill and Offshore Drilling, 2011). At the surface, dispersants were applied sporadically in space and time, based on real-time response to oil slicks. At depth, dispersants were applied directly to the damaged wellhead through a wand inserted into the primary flow of oil and gas. Although the flow of dispersants was not constant, the variability in flow rate was not as large as for the application rate on the surface, and thus average flow rates could reasonably approximate an input of dispersant to the deep ocean (Kujawinski et al., 2011).

With these introductory comments, we start with the basics of the physics and chemistry of dispersants. Oil dispersants are typically solutions containing one or more surfactants (amphiphilic molecules with hydrophilic polar head groups and hydrophobic hydrocarbon-based tails) that partition to the oil-water interface. The surfactants are dissolved in solvent. The role of the surfactant is to reduce the interfacial tension between oil and water. The interfacial tension is a measure of the energy needed to increase the oil-water interfacial area by one unit, defined in units of $J\ m^{-2}$ or $N\ m^{-1}$. Thus, the interfacial tension, γ, can be related to the energy input (W) through $W = \gamma \Delta A$, where ΔA is the increase in the oil-water interfacial area. This equation shows that a reduction in the interfacial tension has the effect of increasing the interfacial area for a given amount of energy input (wave action for surface spills and turbulence associated with deep-sea release). The objective of dispersant systems, therefore, is to lower interfacial tension sufficiently to create droplets that have a diameter of less than about 70 µm. At this size range, the oil droplets stay suspended in the water column (colloidal stability) and do not rise to the surface. The significant increase in surface area of dispersed oil compared to the flat interface of a surface oil slick is thought to allow easier access to oil by oil-degrading bacteria, thus enhancing rates of biodegradation (Lee et al., 2013; Prince et al., 2013; Aeppli et al., 2014; McFarlin et al., 2014; Prince and Parkerton, 2014; Prince and Butler, 2014). However, recent work indicates that dispersants may suppress the activity of oil-degrading microorganisms (Kleindienst et al., 2015a,b). Excellent reviews on dispersants, their effectiveness,

and their ecological impacts are found both in earlier research, as summarized in a National Research Council (2005) report, and in a more recent book summarizing dispersant application for the DWH incident (Judson et al., 2010), with details on dispersant testing for efficacy and toxicity, especially as designed by the US Environmental Protection Agency (EPA). In addition, recent research sponsored by the Gulf of Mexico Research Initiative (GoMRI; http://www.gomri.org) has generated a significant body of literature on the ecological and biological impacts of dispersants.

The most widely used and benchmarked dispersant is the Corexit class of dispersants, particularly EC9500A (hereafter referred to as Corexit 9500), developed by ExxonMobil and manufactured by EcoLab. Corexit 9500 was used in the DWH incident and represented the first instance of dispersants applied to a deep-sea spill at the source of the oil release. Other major classes of dispersants include the Dasic class (Slickgone) made by the Dasic Corporation in the UK, and the Finasol class of dispersants made by Total SA (France). In this paper, we focus on Corexit 9500, which typically contains three surfactant groups, Span 80 (sorbitan monooleate), Tween 80 and Tween 85 (polyoxyethylene (20) sorbitan monooleate), and DOSS (bis (2-ethylhexyl) sodium sulfosuccinate). DOSS (imprecisely expanded as dioctyl sodium sulfosuccinate) is also referred to as AOT or Aerosol OT in the literature on colloidal science, but this is trademark nomenclature, and we will use the term DOSS in this paper. The surfactants are dissolved in solvents, typically propylene glycol and petroleum distillates.

Figure 1 shows structures of the primary surfactant components of Corexit 9500. The Span and the Tweens are nonionic saccharide-based surfactants that are considered to be easily biodegraded due to their easily metabolized

saccharide-containing structures (Place et al., 2016). DOSS is an anionic double-tailed surfactant that could persist for significantly longer periods in the marine environment (Kujawinski et al., 2011; Place et al., 2016). Span is insoluble in water while DOSS is sparingly soluble, but both surfactants are fully soluble in hydrocarbons. The twin-tailed DOSS easily forms reverse micelles, which transition to water-in-oil microemulsions with the addition of small amounts of water. Tweens are fully soluble in water. The roles of the two solvents are not entirely clear, but it is generally accepted that both solvents are used to ensure compatibility with the oil-soluble and the water-soluble surfactants, and are mutually miscible, leading to a single-phase system. Although the exact composition of Corexit 9500 was not disclosed by EcoLab (Nedwed et al., 2008), Place et al. (2016) reported the composition (% w/w) of Corexit 9500 as 18% DOSS, 4.4% Span 80, 18% Tween 80, and 4.6% Tween 85. All of these surfactants are used in other commercial applications,

including cosmetics, textiles, paints, and medicine, but had not been previously applied in large volumes to seawater as dispersants. Place et al. (2016) also found that Corexit 9500 contains 0.28% w/w α- and β-ethylhexyl sulfosucccinate (EHSS); EHSS likely occurs as a synthesis impurity in Corexit 9500, but it is also reported as an abiotic hydrolysis product and biodegradation product of DOSS (Hales, 1993; Campo et al., 2013). The invention of the Corexit class of dispersants is attributed to Gerard P. Canevari at Exxon (McAuliffe et al., 1980; Canevari, 1982; Nedwed et al., 2008) and is a landmark in oil spill remediation technologies. Canevari (1973) developed the idea of blending these three types of surfactants in an organic solvent to apply to the surface of an oil slick on the open sea. This development was stimulated by the need for more effective and more environmentally friendly dispersants after poor experience with detergents (notably, in the Torrey Canyon oil spill off the Cornwall coast in 1968; Canevari, 1973). Corexit 9500 is

stockpiled at various locations along the US coastline and is currently considered the dispersant of choice.

In the remediation of surface spills, dispersant is sprayed down onto the surface of the oil slick, preferably from an airplane (for fast response, and to avoid spreading the slick with boats; see title page photo). In application, it is important for the dispersant to be injected into the oil to enhance surfactant attachment at the oil-water interface. Dispersant application to bulk seawater leads to dilution of the surfactants and a loss of efficacy. After delivery to the oil in surface spills, surfactants must be able to assist dispersion into small droplets with only wave action for mechanical agitation. Dispersants are only effective in situations where weather situations are conducive to wave action. In the DWH incident, dispersant was directly introduced into the jet of oil emanating from the seafloor as well as onto surface slicks. The turbulence generated by fluid dynamics of such jets is sufficient to cause mixing and to break oil globules into smaller droplets.
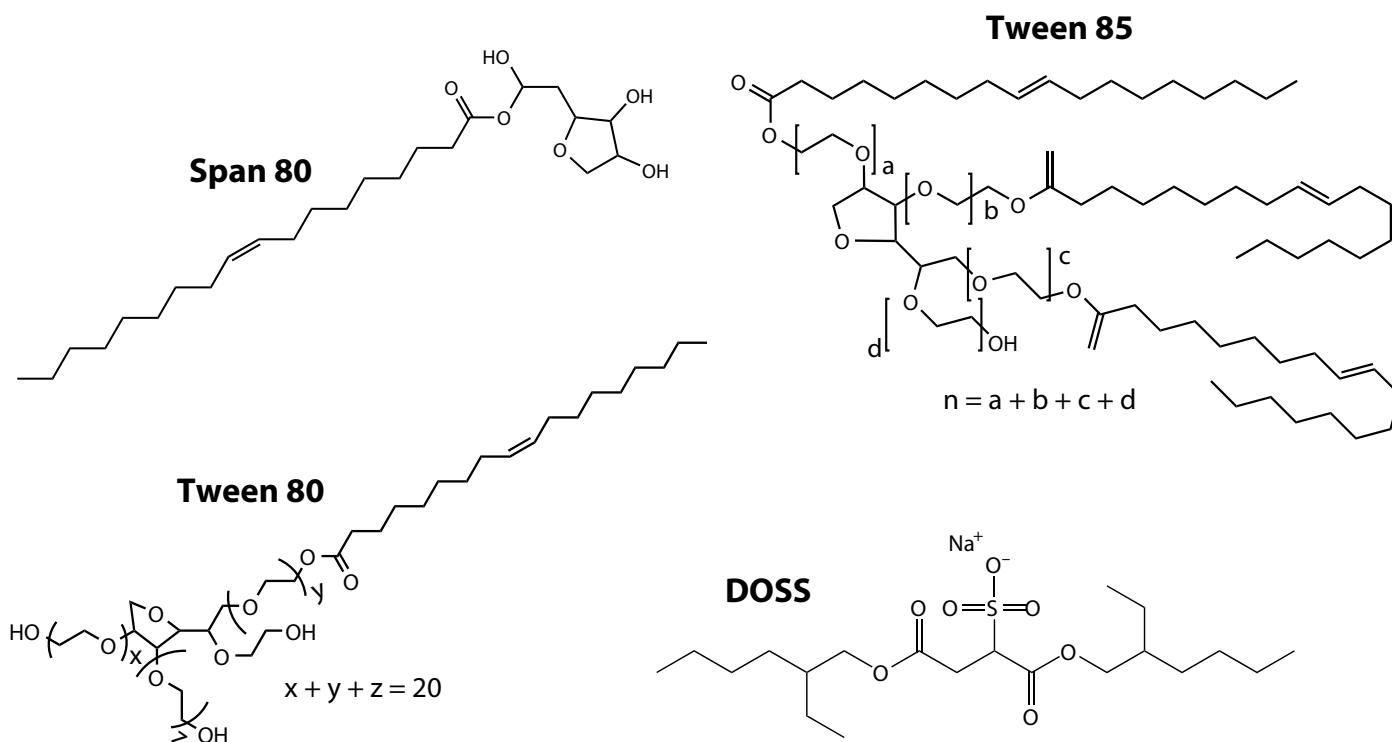

FIGURE 1. Structures of the surfactants used in the formulation of Corexit 9500.

Effectiveness of the dispersant depends strongly on its surfactant composition (Brochu et al., 1986; Brandvik et al. 1998; Riehm and McCormick, 2014), with the optimal mixture of Tween, Span, and DOSS needed for maximum effectiveness defined as accomplishing the greatest reduction in oil-water interfacial tension. Blending surfactants, which each have different hydrophilic-lipophilic-balance (HLB) values, results in an interfacial tension less than 10^{-3} mN m^{-1}, much lower than the interfacial tension achieved using the components of Corexit 9500 individually. The molecular mechanisms of such synergistic effects of the surfactant mixture on interfacial tension remain to be fully understood. However, in dynamics of the dispersion process, low interfacial tension alone may not fully explain effective dispersion composition. One complication is that water-soluble Tween and some DOSS can separate from the interface and leach into the seawater. If this occurs too quickly, then the dispersant-treated oil slick might not maintain a sufficiently low interfacial tension over the time period to complete dispersion. Although Span (being very oil soluble) will tend to stay in the oil, too much Span actually degrades dispersion effectiveness (Riehm and McCormick, 2014), even when the interfacial tension is quite low. This behavior might reflect the fact that sufficient hydrophilic components are needed to maintain a low interfacial tension. Rates of diffusion of different components in the oil phase onto the surface of a droplet can also affect the dispersion process. As new droplets are being created, the breakup rate can become limited to being only as fast as the rate at which surfactants are able to populate the new surfaces. (Riehm and McCormick, 2014).

Packing of surfactants at the oil-water interface is of significant relevance in achieving low interfacial tensions and in maintaining such tensions. A very interesting set of dynamic interfacial tension experiments by Reichert and Walker (2013) showed that the Tweens appeared to create a stable monolayer at the interface even under bulk dilution, leading to a thermodynamically irreversible adsorption at the interface. This result is rather unexpected, because surfactants have finite partition coefficients between the interface and the continuous bulk water phase where they exist as monomers at concentrations lower than the critical micellar concentration. Reducing the bulk concentration to infinitely dilute levels is expected to lead to surfactant partitioning away from the interface and into the bulk to maintain the value of the partition coefficient. Molecular simulation by Tang et al. (2014) indicates that the large hydrophilic head groups of Tween may lead to entanglements at the oil-water interface, preventing desorption back into seawater, thus explaining the irreversibility of adsorption observed by Reichert and Walker (2013). Implications of this finding include the possibility that the cooperative interaction of this irreversible monolayer with Span and DOSS might also play a role in the compositional dependence of dispersant effectiveness. Figure 2 illustrates the various surfactant components at the oil-water interface (Riehm and McCormick, 2014).
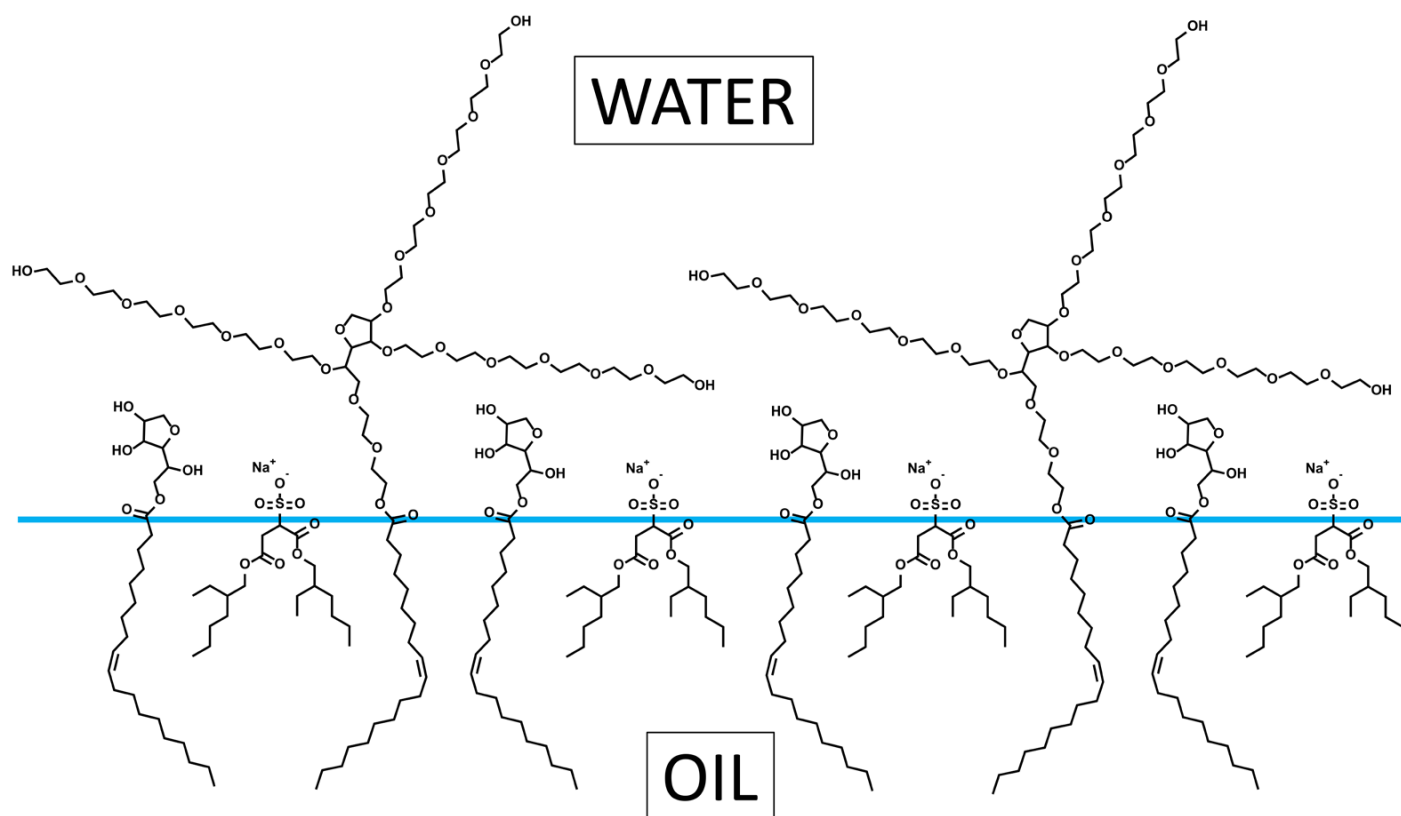
FIGURE 2. Representation of the surfactant components of Corexit 9500 at the oil-water interface. *Reproduced from Riehm and McCormick (2014)*

DISPERSANT FATE AND ECOSYSTEM IMPACT

Mitigating the impact of oil on nearby coastal areas was a primary concern during the DWH oil spill. Once dispersants were applied, it was imperative to assess the fate of these mixtures in order to estimate their impact on water quality and environmental health. Unfortunately, appropriate sample analysis protocols were not in place during the DWH inci-

the impact of Corexit 9500 on the biodegradation of oil (Kleindienst et al., 2015b).

During DWH and afterward, analyses of surfactants from the dispersant focused on DOSS in the deepwater plume rather than on surface samples. The few studies that included surface samples showed nearly universal low (or non-detectable) concentrations of DOSS in surface waters (Gray et al., 2014). In contrast, samples collected in the oil-derived

surfactants Span 80 and Tweens 80 and 85 showed little long-term presence of these molecules in deep waters (McAuliffe et al., 1980). This is likely due to analytical difficulties and rapid degradation in non-fixed seawater samples (Place et al., 2016). In summary, work to date suggests that the Corexit 9500 component DOSS was transferred to the deepwater plume. Once in the plume, DOSS was transported along deepwater currents until dilution reduced concentrations of DOSS below the detection limits.

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dent to quantify the components of dispersants in seawater (Place et al., 2010). However, the two Corexit formulations were chemically similar in their surfactant compositions, enabling the rapid development of protocols that would track surfactants from both dispersants. Place et al. (2016) developed a method to analyze the surfactant components in seawater, based on large volume injection (which takes minimal sample preparation) liquid chromatography coupled to mass spectrometry. This method is advantageous because it is able to quantify all four components of Corexit 9500 in one analysis. In the case of DOSS, more targeted methods were also developed for higher sensitivity analyses (Kujawinski et al., 2011; Gray et al., 2014). All methods were able to detect DOSS below the EPA limit of concern of 20 μg L^{-1} (Kujawinski et al., 2011; White et al., 2014). In the years since the DWH spill itself, these and other complementary methods have been applied in order to monitor the fate of surfactants in Corexit 9500 and to assess

plume contained appreciable DOSS. Near the wellhead during the blowout, concentrations of DOSS were correlated with dissolved methane concentrations and fluorescence-based measurements of hydrocarbons (Kujawinski et al., 2011). Samples from shallower depths contained no detectable DOSS, suggesting that DOSS was transferred quantitatively into the dissolved oil plume after injection at the wellhead. As the plume traveled farther from the wellhead, DOSS concentrations decreased primarily by dilution (Kujawinski et al., 2011) rather than by biological degradation. Subsequent experiments showed that DOSS does not degrade appreciably under the cold and dark conditions of the deep ocean (Campo et al., 2013). Measurements of α-EHSS and β-EHSS in open seawater could not be interpreted as unambiguous evidence of DOSS biodegradation because α-EHSS and β-EHSS occur in Corexit 9500 as a synthesis impurity (Barsamian et al., 2014; Place et al., 2016). Complementary analyses of the nonionic

Most of the work on dispersants used in the DWH spill focused on the water column because it appeared that the bulk of the DOSS measured occurred in this large reservoir. However, there is now evidence that DOSS was entrained in oil that rose to the surface or sank into sediments near the damaged wellhead (White et al., 2014). White et al. (2014) detected DOSS in surface sediments and on corals near the damaged wellhead. Concentrations were spatially heterogeneous, suggesting stochastic delivery of dispersants to the ocean floor, perhaps as part of marine oil snow, as discussed below. These samples were collected within six months of capping of the wellhead, but a more comprehensive survey shows that DOSS concentrations remained high for the following four years (Perkins and Field, 2014). Nearly four years after the spill, DOSS was detected within oil-sand patties collected from beaches along the Gulf of Mexico (White et al., 2014). Composition of oil in the inner portion of the patties confirmed the source of the patties as DWH-released Macondo oil. Because DOSS is more water-soluble than petroleum hydrocarbons, its persistence within these patties suggests that at least part of each patty was not in contact with the surrounding water (White et al., 2014). Although DOSS concentrations in these matrices are exceedingly small, they highlight the pervasive contamination of the Gulf of Mexico by the DWH oil spill and the challenges associated with removal of all oil and the surfactants from dispersants from the ecosystem.

During the course of the DWH oil spill, abundant marine oil snow formed at the sea surface. These macroaggregates contain organic matter, oil, and bacterially produced EPS (extracellular polymeric substances; Gutierrez et al., 2013) that help bind the particles together (Passow et al., 2012; Ziervogel et al., 2012). Bacterially derived EPS facilitates access to oil components and concurrently serves as a metabolic substrate for the diverse community of γ- and α-*Proteobacteria*, *Bacteroidetes*, and *Planktomycetales* associated with these marine oil snow aggregates (Arnosti et al., 2016). Much of the oil that eventually vanished from the surface ocean is hypothesized to have been removed via sinking of the marine oil snow once its density exceeded that of seawater (Passow et al., 2012; Passow and Ziervogel, 2016, in this issue). Figure 3 illustrates a laboratory experiment demonstrating the formation of marine oil snow (Ziervogel et al., 2012).

The observation that microbially mediated aggregation and degradation processes affected the dynamics of oil at the sea surface raises questions about effects of dispersant application on microbial activities and microbially catalyzed degradation of oil. Application of dispersant at the broken riser pipe at a depth of 1,500 m likely contributed to the formation of a plume of dispersed oil at depths of ~1,100–1,200 m (Camilli et al., 2010). This plume harbored a distinct microbial community enriched in the γ-Proteobacterial order *Oceanospirillales* (Hazen et al., 2010). After the riser pipe was plugged, the plume was no longer detectable; the specific fate of the plume, and the role of microbial communities in processing the escaped oil, are a focus of considerable study.

Efforts to understand specific effects of dispersant application, particularly at depth, has spurred further investigations of microbial communities and their activities. Microbial communities deep in the Gulf of Mexico metabolized a considerable fraction of the spilled oil

(Lu et al., 2012). Bacteria enriched at 5°C on Corexit 9500 and Macondo oil, using uncontaminated water samples collected at a depth of 1,100 m near the spill site, were found to remove 25% and 60% of the dissolved oil without and with addition of Corexit 9500, respectively (Bælum et al., 2012). Straight-chain alkanes, as well as Corexit 9500, were readily degraded in these incubations. Large oil-snow flocs also were observed; the microbial community associated with the flocs were dominated by *Colwelliaceae* (Bælum et al., 2012). The *Colwellia* strain RC25 isolated from these incubations proved capable of degrading 75% of the Macondo oil in the presence of Corexit 9500 (Bælum et al., 2012). The effect of droplet size was also found to affect biodegradation of oil, as demonstrated using oil collected from the riser pipe in May 2010 and Corexit 9500. These experiments, carried out with water collected from a Norwegian fjord, showed that smaller oil droplet size correlated with faster biodegradation rates (Brakstad et al., 2015).

Application of dispersants, however, may affect the growth and composition

of the natural microbial community, as suggested by experiments conducted using deep water from a natural oil seep in the Gulf of Mexico incubated with the water-accommodated fraction (containing no dispersant) and chemically enhanced water-accommodated fraction (with dispersant) of Louisiana sweet crude oil. The composition of the microbial community at the end of the incubations differed: incubations including dispersant had high abundance of *Colwellia*, whereas incubations without dispersant were dominated by *Marinobacter* (Kleindienst et al., 2015b). Dispersant-only incubations (lacking the water-accommodated oil fraction) also showed enhanced *Colwellia* abundance, with different *Colwellia* taxa dominating the dispersant-only and the dispersant and water-accommodated oil experiments. Moreover, degradation rates of hexadecane and naphthalene were more rapid in the absence of dispersants, as was the overall removal of the water-accommodated oil fraction (Kleindienst et al., 2015b). Selective effects of dispersant on degradation of specific components of

FIGURE 3. Marine oil snow formed after incubation of uncontaminated surface seawater from the Gulf of Mexico with spilled Deepwater Horizon oil collected at the sea surface near the spill site in early May 2010. This photo shows the marine oil snow hanging suspended from the surface interface after 21 days of incubation on a roller table. The marine oil snow contains active bacteria, sticky bacterially derived extracellular polymeric substances, and distinct droplets of oil (dark spheres). *Photo from Ziervogel et al. (2012)*

10 mm

oil have also been reported for Alaskan North Slope oil and Corexit 9500: hexadecane and phenanthrene were mineralized less in the presence of dispersant, but dodecane and naphthalene degradation did not show any effect from the presence of dispersant (Lindstrom et al., 2002). Corexit 9500 itself was also found to support considerable microbial growth, but it did not increase min-

> [V]ariable effects of Corexit 9500 on microbial isolates and microbial communities and their oil-degrading capabilities have been observed, depending in large part on the nature and state of the oil (weathered or not), relative ratios of oil and dispersant, and the composition of the in situ microbial community.

eralization of either fresh or weathered Alaskan North Slope oil (Lindstrom et al., 2002). Moreover, Corexit 9500 was found to be toxic to specific bacteria, including *Marinobacter* and *Acinetobacter* isolates obtained from DWH oil-contaminated beach sands (Hamdan and Fulmer, 2011). Further study into the fundamental mechanisms of surfactant-marine bacteria interactions is clearly required to understand such toxicity.

Whether marine oil snow formed at depth in the plume at the time of the oil spill is not clear (Passow et al., 2012), although Hazen et al. (2010) reported "cellular flocs" in the deepwater plume. Experimental investigations using deep Gulf of Mexico water have reported formation of marine oil snow in treatments with oil, whether or not dispersant is present (Bælum et al., 2012; Kleindienst et al., 2015b). Likewise, investigations with coastal surface seawater, Louisiana

sweet crude oil, and Corexit 9500 yielded marine oil snow, also in the presence of dispersant; the marine oil snow formed in the presence of dispersant that contained more *n*-alkanes than the oil-only incubations (Fu et al., 2014). Other experiments with plume and non-plume deep water, however, showed variable formation of marine oil snow, potentially due to differences in deepwater microbial

community composition, which changed with time and space (Passow et al., 2012). Systematic investigations using seawater from above natural oil seeps in the Gulf of Mexico as well as from the Santa Barbara Basin highlighted the effects of oil weathering (in particular, exposure to UV light) as a factor enhancing marine oil snow formation (Passow, 2014). In these investigations, the presence of Corexit 9500—particularly at low concentrations—reduced or inhibited marine oil snow formation, although high Corexit 9500 concentrations (1 mL L^{-1}) led to aggregate formation (Passow, 2014). In summary, variable effects of Corexit 9500 on microbial isolates and microbial communities and their oil-degrading capabilities have been observed, depending in large part on the nature and state of the oil (weathered or not), relative ratios of oil and dispersant, and the composition of the in situ microbial community.

NEW DEVELOPMENTS AND IMPLICATIONS IN DISPERSANT DESIGN AND IMPLEMENTATION

Although Corexit 9500 is currently the dispersant of choice, there are ongoing issues regarding its use, and there is the potential for improvement. First, liquid phase dispersants may not work well on weathered oil and are easily washed away by wave action when applied onto weathered oil. Second, the dispersant that does not directly fall on an oil slick is not effective, and may have unintended deleterious effects on microbial communities. There is also concern that solvents used in dispersant formulations, although relatively innocuous in comparison to the polycyclic aromatic hydrocarbons (PAHs) in the oil phase, constitute an additional and perhaps significant insertion of hydrocarbons to the environment. Lastly, the degree to which microorganism attachment to oil droplets and the degree to which formation of biofilms are facilitated or hindered by surfactants at the oil-water interface both remain poorly constrained. However, replacement of Corexit 9500 and its variants from Dasic and Total with entirely different dispersants is unlikely due to the logistics of large-scale manufacture, rapid deployment, toxicity testing, and approval procedures from the appropriate federal agencies, including the EPA and the National Oceanic and Atmospheric Administration (NOAA).

There are opportunities, however, for new dispersants that work in synergy with current dispersants and mitigate some of their disadvantages. For example, dispersants that adhere to weathered oil and cause the oil to disperse, perhaps by breaking up the water-in-oil emulsions present in such systems, would be relevant. Indeed, there is recent work by ExxonMobil to develop gel-type dispersants for such applications (Nedwed et al., 2008). Key beneficial characteristics of gel-type dispersants over traditional liquid dispersants include (a) close adherence to weathered oils without being washed off, (b) extended buoyancy periods that allow

more contact with oil, (c) high surfactant concentrations, (d) reduced solvent levels, and (e) possibility of the gels providing some degree of visible feedback to oil spill responders (Nedwed et al., 2008).

Athas et al. (2014) pioneered a system containing soybean lecithin and the surfactant Tween 80 dissolved in ethanol, showing that this formulation leads to effective emulsification. Substitution of the double-tailed phospholipids in lecithin for DOSS, which is the persistent component in Corexit 9500, is a significant finding, as naturally occurring phospholipids are likely to be environmentally benign. Additional research on the use of lecithin as a substitute for DOSS has been carried out by Riehm et al. (2015) and by Nyankson et al. (2015a).

Use of particle-stabilized emulsions is also being studied intensively as a way to stabilize emulsion droplets against coalescence, thus complementing the role of dispersants. The ability of particles to partition to the oil-water interface and stabilize emulsions is a much studied phenomenon often referred to as Pickering emulsions, following early pioneering studies by Ramsden (1903) and Pickering (1907). Several experimental and theoretical studies have been carried out on solids-stabilized emulsions in order to understand factors that affect stability and structure of the interface (Binks and Lumsdon, 2000; Ingram et al., 2010). Examples include use of carbon-based particles and silicas (Creighton et al., 2014; Rodd et al., 2014). We also note the relevance to oil-mineral aggregates, a significant topic related to understanding the fate of oil droplets when they come into contact with sediment particles (Passow et al., 2012; Gong et al., 2014). The attachment of sediments to such droplets at the oil-water interface is clearly a consequence of the thermodynamics of particle-stabilized droplets, where the energy to remove particles from the oil-water interface is several orders of magnitude above the thermal energy. Although particulate systems are effective at stabilizing emulsions, they do not decrease the

oil-water interfacial tension significantly and are therefore ineffective as dispersants. Owoseni et al. (2014) used a tubular particulate system made of halloysite, a natural clay type mineral where the tube lumen is loaded with dispersant surfactant components (Tween, Span, and DOSS) (see also Athas et al., 2014; Nyankson et al., 2015b). If targeted correctly, these particles attach to and deliver the surfactant to the oil-water interface, lowering the oil-water interfacial tension and breaking up the oil into smaller droplets. Figure 4 illustrates attachment of

halloysite nanotubes on oil droplets.

Finally, there is a need to develop safe materials for efficient chemical herding, a related process that uses surfactants at the air-water interface to compact oil slicks into layers (at least 2–3 mm) that are sufficiently thick to enable burning of the oil or facilitate surface skimming (Buist et al., 2011). Herding is especially relevant in the Arctic where the presence of ice floes dampens wave action that aids in dispersing oil, and dispersant application is ineffective due to indiscriminate spraying on ice. The development of new plant-based
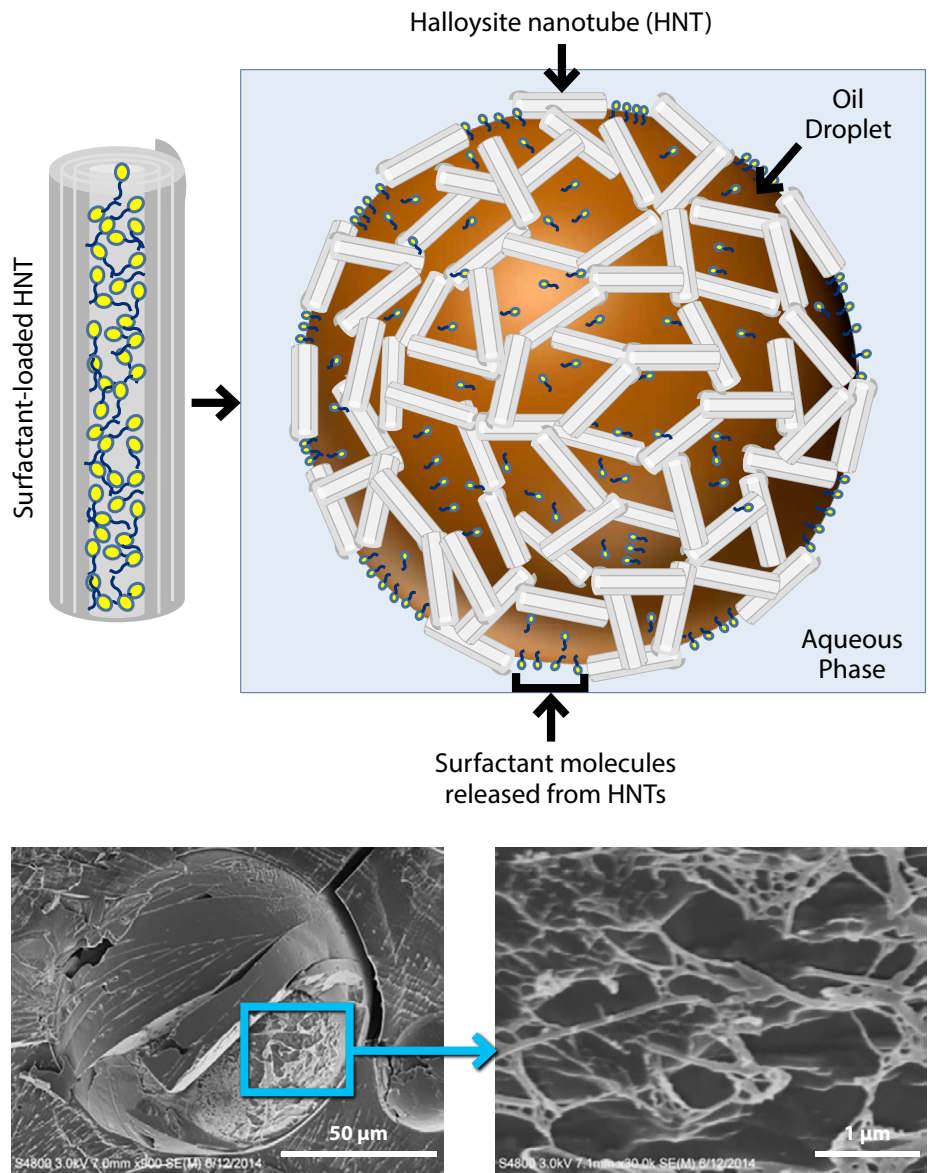
FIGURE 4. (top) Schematic of halloysite clay nanotube (HNT) stabilization of an emulsion droplet and the release of surfactant cargo. (bottom) Cryo scanning electron microscope image showing an oil droplet stabilized with HNT on the left, and a magnified view on the right showing the network of HNT on the oil-water interface. *Reproduced from Owoseni et al. (2014)*

amphiphiles for herding (Gupta et al., 2015) may be extended to use of such materials in the development of environmentally benign surfactants that may also have applications as dispersants.

CONCLUDING REMARKS

We conclude by stating some specific cautionary recommendations on dispersant research. We cannot make clear delineations regarding use of dispersants, as guidance for their use involves a number of factors related to oil spills (surface or deep-sea spill, temperature and wind conditions for surface spills, proximity to coastlines and the nature of seafloor terrain, sensitivity of the ecosystem to chemical perturbations). But we do recognize that it is extremely important to conduct laboratory research at concentrations and under conditions relevant to marine environments. In a laboratory setting with experimental systems of finite volume, replicating the vast dilution of the marine environment is difficult. With these dispersant systems, surfactants at the oil-water interface exist in equilibrium with surfactant in the bulk water phase. In such closed systems, it may not be surprising that microorganism viability is affected by the presence of surfactants, as bacterial membranes may suffer disruptions due to surfactant tail insertion, a well-known aspect of the use of soaps. Thus, experiments involving continuous removal of surfactants in bulk are important to understanding dispersant action. Additionally, the effects of exposure of organisms to dispersants and oil droplet concentrations depend on the specific organisms under consideration. Marine microbial communities are highly diverse, and their compositions and activities are variable with time and space in the ocean; as discussed above, the presence and abundance of oil, dispersants, and secondary metabolites can greatly affect the growth and activity of these organisms. Moreover, for oil-degrading microorganisms that migrate to the oil-water interface, the local concentration of surfactants at the oil-

water interface is an important determinant of exposure. Future research that couples greater insights into microbial capabilities and responses with higher-resolution physicochemical definition of interfaces and dispersant gradients will greatly contribute to our understanding of the impact of dispersants on microbial communities. ⌾

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